Low Electrical Field Characteristics of Piezoelectric Ceramic Rings, Part II

S. W. MEEKS AND R. W. TIMME

Standards Branch
Underwater Sound Reference Division

1 May 1975



NAVAL RESEARCH LABORATORY Underwater Sound Reference Division P. O. Box 8337, Orlando, Fla. 32806

Approved for public release; distribution unlimited.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION	READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER	3. RECIPIENT'S CATALOG NUMBER	
NRL Report 7891		
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
LOW ELECTRICAL FIELD CHARACTERIST	TICS OF	This is an interim report
PIEZOELECTRIC CERAMIC RINGS, PART	II :	on the problem 6. PERFORMING ORG. REPORT NUMBER
		o. PERFORMING ONG. NO. ON HOMBEN
7. AUTHOR(a)		8. CONTRACT OR GRANT NUMBER(#)
C to Marke and D to minus		
S. W. Meeks and R. W. Timme		
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Underwater Sound Reference Divisi	on	NRL Problem S02-31
P.O. Box 8337, Orlando, Fla. 3280)6	RF 11-121-403-4472
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
Office of Naval Research		1 May 1975
Department of the Navy		13. NUMBER OF PAGES
Arlington, Va. 22217	iii + 20	
14. MONITORING AGENCY NAME & ADDRESS(II differen	15. SECURITY CLASS. (of this report)	
	UNCLASSIFIED	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA	
16. DISTRIBUTION STATEMENT (of this Report)		I NA

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the electrect entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Piezoelectric ceramics Sonar transducers Military standards

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Low electrical field parameters of Type I piezoelectric ceramic rings purchased from four major suppliers of sonar ceramic elements were measured to determine the applicability and value of MIL-STD-1376(SHIPS), "Piezoelectric Ceramic for Sonar Transducers." Data are also presented on two recently developed low-aging compositions. Measured values of the relative dielectric constant, loss tangent, electromechanical coupling factor, frequency constant, mechanical \boldsymbol{Q}_{m} , elastic compliance coefficient, and piezo-

UNCLASSIFIED

DECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20.	(Conti	ทแคสโ

electric constants at low electrical fields and as functions of temperature (0 to 50°C) and aging are presented. The samples of Type I ceramic showed some improvement toward satisfying all the specifications of MIL-STD-1376 (SHIPS) over those previously measured. The low-aging compositions are characterized as a function of temperature and are shown to be similar to the Type I composition.

Contents

Intr	oduction			1
	surement Theory			
	erimental Technique			
	ılts and Discussion			
	alusions			
Ty	pe I Ceramic			17
Lo	nw-Aging Ceramics			18
Ackn	nowledgments			18
Refe	erences			19
Appe	endix A			20
	Figures			
•				
1.	Block diagram of experimental apparatus			
2.	Relative dielectric constant K_{33}^{T} as a function of temperature	϶.	•	8
3.	Loss tangent or dissipation factor $tan \ \delta$ as a function of temperature			ρ
4.	Effective electromechanical coupling factor k as a	-	_	
5.	function of temperature		•	9
6.	Mechanical Q as a function of temperature			11
7.	Elastic compliance coefficient s as a function of			
8.	temperature	•	•	11 12
9.	Piezoelectric constant g_{31} as a function of temperature			
10.	Aging of relative dielectric constant K_{33}^{T}		•	14
•	33			
	Tables			
I.	Physical dimensions of ceramic rings at 24°C		_	6
II.	Piezoelectric characteristics of ceramic rings		•	7
III.	Elastic compliance coefficient and piezoelectric constants of piezoelectric ceramic samples			10
IV.	Approximate percent change of parameters with			
٧.	temperature, 0-50°C	•	•	13
	Type I ceramic samples			15
VI.	Approximate aging rates and ten-day values, low-aging compositions	_		16

LOW ELECTRICAL FIELD CHARACTERISTICS OF PIEZOELECTRIC CERAMIC RINGS, PART II

Introduction

This is the second of a series of NRL Reports on the evaluation of commercially supplied piezoelectric ceramic materials used as acoustic elements in sonar devices. The first report of the series [1] indicated that the low electrical field parameters of piezoelectric ceramic rings from six major suppliers generally failed to satisfy all the requirements of the applicable military standard MIL-STD-1376(SHIPS) [2]. Similar findings reported by other investigators [3,4,5,6] emphasized the need for better quality control by the manufacturers and indicated the desirability of checking the characteristics of any additional materials acquired under the military standard.

In continuation and extension of the materials evaluation program reported by Timme [1], additional piezoelectric ceramic elements were purchased in 1974 in accordance with the military standard. The shape and characteristics of the ceramic elements were selected on the basis of unambiguous interpretation of results. The shape chosen was a cylindrical ring, axially poled, and of dimensions such that a pure hoop resonance mode was far removed from other resonance modes. One of the ceramic materials obtained was the Type I lead titanate-zirconate composition that is widely used in sonar devices. Two additional ceramic compositions were purchased for general measurements and comparison of results with those obtained for the Type I composition. These two ceramics were developed independently by Honeywell Ceramics Center [7] and Vernitron Piezoelectric Division [8] under Naval Sea System Command contracts for the development of low-aging sonar materials with improved stability to compressive stress of 69 MPa (10,000 lb/in.²) and to driving fields up to 4 kV/cm.

The composition of the Honeywell low-aging ceramic is given in reference [7] as $(Pb.94^{Sr}.06).980$ $(Zr.51^{Ti}.49).995^{Cr}.015^{Mn}.005^{O}3$, and that of the Vernitron ceramic is given in reference [8] as $Pb.94^{Ca}.05^{Mg}.01^{(Zr.52^{Ti}.48)}.97^{Cr}.02^{Fe}.01^{O}3$.

The results reported here are based on data taken from a total of 82 ceramic rings from four companies. Twenty-four Type I rings were from Gulton Industries, 16 from Channel Industries, 8 from Vernitron Piezo-electric Division, and 16 from Honeywell Ceramics Center. Nine low-aging ceramic rings were provided by Vernitron and nine were provided by Honeywell.

The purpose of this report is to present the results of measurements at low applied field of the parameters of ceramic rings and their variations with temperature and time, and to compare their performance with the requirements of MIL-STD-1376(SHIPS). This report is also concerned with the variation of the parameters among the products of various manufacturers and with any improvements in the ceramics over those previously investigated by Timme [1].

Measurement Theory

The object of this section is to point out the measurable quantities and the equations relating measurable quantities to desired quantities. The vibrating piezoelectric ring can be described by the well-known theory of the driven, damped harmonic oscillator [1,9]. Harmonic oscillator theory and the piezoelectric equations of state give the expression for the admittance of a ceramic ring:

$$Y = \frac{\omega^2 \omega_0^2 a C_1}{(\omega_0^2 - \omega^2)^2 + a^2 \omega^2} + j\omega \left[\frac{\omega_0^2 (\omega_0^2 - \omega^2) C_1}{(\omega_0^2 - \omega^2)^2 + a^2 \omega^2} + C_0 \right], \quad (1)$$

where ω is the driving frequency, ω_0 is the resonance frequency, a is a damping coefficient that may consist of an external loading as well as an internal resistance to strain and can be a function of frequency, C_1 is the motional capacitance, and C_0 is the clamped capacitance. The second term of Eq. (1) becomes zero at the antiresonance frequency, which leads to the electromechanical coupling coefficient

$$k_{eff}^2 = (\omega_a^2 - \omega_0^2)/\omega_a^2.$$
 (2)

The expression for Q_m , the mechanical quality factor, can be obtained from the conductance G at ω_0 and the fact that $Q_m = \omega_0/a$. Thus

$$Q_{\rm m} = G(\omega_0)/\omega_0 c_{\rm f} k_{\rm eff}^2, \tag{3}$$

where $C_{\underline{f}}$ is the free capacitance far from resonance.

The relative dielectric constant is obtained from the free capacitance with

$$K_{33}^{T} = C_{f} t/A \epsilon_{0}, \qquad (4)$$

where t is the thickness (between electrodes), A is the surface area of the ceramic electrodes, and ϵ_0 is the permittivity of free space.

The two piezoelectric constants \mathbf{d}_{31} and \mathbf{g}_{31} are calculated from the following expressions:

$$d_{31} = \frac{k_{eff}}{\omega_0} \left(\frac{4tC_f}{\rho \pi w D_m}\right)^{\frac{1}{2}}$$
 (5)

and

$$g_{31} = d_{31}/K_{33}^{T} \varepsilon_{0}, \tag{6}$$

where w is the wall thickness, ρ is the density, and \textbf{D}_{m} is the mean diameter of the ring.

The elastic compliance coefficient is

$$s_{11}^{E} = 4/\rho D_{m}^{2} \omega_{0}^{2}, \tag{7}$$

and the frequency constant is obtained from

$$N = \omega_0 D_m / 4. \tag{8}$$

The dielectric dissipation $\tan \delta$ is also a parameter of interest that can be measured directly.

The measurable quantities are:

 ω_{Ω} , the resonance frequency

 ω_{a} , the antiresonance frequency

G (at $\omega = \omega_0$) = 1/R (at $\omega = \omega_0$), the conductance at resonance

 $\mathbf{C}_{\mathbf{f}}$, the free capacitance far from resonance

tan δ , the dielectric dissipation

t, thickness of the rings (between electrodes)

w, wall thickness of the ceramic

 D_{m} , mean diameter of a ring

m, mass of a ceramic ring

The resulting parameters of interest are:

 Q_m , the mechanical quality factor

 $\mathbf{k}_{\mbox{eff}}$, the electromechanical coupling coefficient

 K_{33}^{T} , the relative dielectric constant under constant stress

N, the frequency constant

 s_{11}^E , the elastic compliance coefficient at constant electric field d_{31} , a piezoelectric constant g_{31} , a piezoelectric constant tan δ , the dielectric dissipation ρ , density of a ceramic material

Experimental Technique

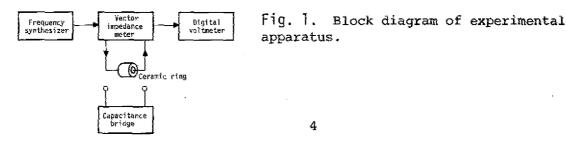
Physical dimensions and mass were measured only at room temperature (24°C) with a Helios precision micrometer and a Mettler analytical balance. Changes in physical dimensions in the temperature range 0 to 50°C are at the limits of detection and may be neglected.

The experimental apparatus used in this program is shown schematically in Fig. 1. The cable capacitance between the ceramic ring and the vector impedance meter (Hewlett-Packard Model 4800A) must be maintained at a very low level in comparison with that of the ceramic ring because of the effect of cable capacitance that lowers the antiresonance frequency $\boldsymbol{\omega}_a$. The value was kept to 25 pF by using a short, low-capacitance cable.

The values of C_f , tan δ , ω_0 , ω_a , and $Z(\omega_0)$ were desired for the ceramic ring uninfluenced by external loading. To minimize this loading, the ring was suspended from a single point by a slender rubber band. Electrical contact was made with the electroded surfaces by a solder joint with a flexible 0.02 mm-diameter silver alloy wire. Variations of the parameters with temperature were determined from values measured for rings stabilized to within $\pm 2^{\circ} C$ in a freezer or an oven. A large quantity of desiccant was used in the freezer to maintain low humidity during measurements.

Free capacitance and loss tangent were measured directly on a capacitance bridge (General Radio Model 1615-A) at 1000 Hz with an excitation field of 0.8 V/cm. This arrangement satisfied the conditions of an electrical field that is low in comparison with the poling field and a frequency far from resonance.

Resonance and antiresonance frequencies were determined from digital readouts of the frequency synthesizer (Hewlett-Packard Model 3320A). The impedance at resonance was displayed by the digital voltmeter (Data Precision Model 2240) upon receiving the calibrated analog output of the



vector impedance meter. Care was taken to choose an impedance measuring device that applied a small electric field to the ring at resonance so that the response of the ring would be linear. The electric field applied at resonance was 2 mV/cm.

Measurements of the various parameters involved the following estimated degrees of uncertainty:

physical dimensions	±0.003 cm (±0.001 in.)
mass	±0.1 gram
$^{\mathrm{C}}_{\mathrm{F}}$	±0.1%
tan δ	±5.0%
$\omega_0/2\pi$	±1 Hz
ω _a /2π	±3 Hz
z(ω ₀)	±5%

On the basis of these uncertainties, all results presented in the next section have associated error bars for which the appropriate values are:

physical dimensions D_{m} , h, t	± 0.003 cm (± 0.001 in.)
density ρ	±0.7%
relative dielectric constant K_{33}^{T}	±0.7%
loss tangent, tan δ	±5.0%
frequency constant N	±0.05%
electromechanical coupling	
factor k	±0.03%
mechanical Q _m	±5%
elastic compliance coefficient s ^E ₁₁	±0.8%
piezoelectric constant d	±0.8%
piezoelectric constant g ₃₁	±1.5%

All data were averaged statistically by material type and manufacturer; results are reported in terms of mean values and, as appropriate, are accompanied by the standard deviations.

Results and Discussion

The characterizations of the rings from the different sources are coded with the letters A, C, D, and E, consistent with the coding used earlier [1,3,4,5,6]. The letters K and L refer to manufacturers of the low-aging compositions. The key to the code is given in Appendix A.

Table I. Physical dimensions of ceramic rings at 24°C.

	Mean diameter		Heig	Height		ness	Density		
Manufacturer	(in.)	Std. dev.	(in.)	Std. dev.	(in.)	Std. dev.	(g/cm ³)	Std. dev.	
А	2.247	0.001	0.505	0.001	0.252	0.001	7.494	0,059	
C	2.246	.001	.503	.001	.252	.001	7.531	.038	
D	2.246	.001	.503	.001	.252	.001	7,444	.043	
E	2.247	.001	.502	.001	.251	.001	7.577	.035	
K*	2.248	.001	.503	.001	.251	.001	7.337	.044	
L*	2.247	.001	.500	.003	.252	.001	7.405	.067	
MIL-STD-1376	2.250±	0.005	0.500±	0.002	0.250±	0.003	7.550 mi	inimum	

^{*}Low-aging piezoelectric ceramic composition.

Table 1 presents the physical dimensions and densities of the rings. The mean diameter of each group is less than the 2.250 in. (5.715 cm) specified by the military standard but falls within the tolerance limits. Mean heights exceed the specified maximum value in four of the six groups. Thicknesses are somewhat above the specified value of 0.250 in. (0.635 cm) but within tolerance limits. Three of the four Type I compositions border on the minimum density requirement of the standard; however, it has been suggested [6] that the minimum density specification be reduced to

7.50 g/cm³, which would permit all but two of the Type I groups to satisfy this part of the standard. The two low-aging compositions are notable in that their densities are significantly lower than the minimum value specified by the military standard.

Results of measurements of the basic parameters K_{33}^T , tan δ , k_{eff} , N, and Q_{m} are presented for Type I and low-aging compositions in Table II and Figs. 2-6. Although values of the parameters s_{11}^E , d_{31} , and g_{31} are not specified in the standard, measured values are presented in Table III and Figs. 7-9 for general information and comparison purposes.

The temperature variations of the measured parameters are apparent from Figs. 2-9. These curves have the same general form as those of earlier measurements [1] and show a similar spread of values and temperature rates of change for rings from several manufacturers. These differences are probably attributable to slight differences in the material formulations and manufacturing techniques. The data points corresponding to each group of rings generally can be joined by a smooth curve.

Table II. Piezoelectric characteristics of ceramic rings.

Temp	Source	т к ₃₃	Std. dev.	tan δ	Std. dev.	k _{eff}	Std. dev.	N (Hz•m)	Std. dev.	Q _m	Std. dev.
4	A	1470	44	0.0032	0.0005	0.3368	0.0157	1585	11	538	82
	C	1168	24	.0022	.0010	.3167	.0083	1679	6	954	147
	D	1094	20	.0019	.0007	.3360	.0064	1630	4	825	89
	E	1127	10	.0013	.0006	.3265	.0023	1691	2	1234	68
	K*	1172	45	.0129	.0053	.2696	.0076	1684	18	511	134
	L*	1130	8	.0042	.0010	.2736	.0018	1678	2	565	40
12	A	1478	33	.0023	.0006	.3364	.0102	1593	10	688	
	C	1173	22	.0014	.0002	.3156	.0067	1683	5	1150	
	D	1153	43	.0013	.0002	.3343	.0025	1639	3	1222	
	E	1144	13	.0011	.0002	.3274	.0022	1693	2	1472	
	K*	1201	33	.0122	.0053	.2682	.0086	1684	15	549	
	L*	1142	8	.0039	.0001	. 2726	.0027	1682	3	577	43
24	A	1487	41	.0019	.0003	.3366	.0115	1600	10	764	60
	С	1193	21	.0014	.0001	.3157	.0083	1688	4	1277	127
	D	1124	17	.0012	.0001	.3398	.0029	1640	3	1214	
	E	1166	11	.0012	.0003	.3301	.0019	1695	2	1531	29
	K*	1222	40	.0148	.0092	.2670	.0158	1688	14	506	197
	L*	1160	7	.0047	.0005	.2726	.0040	1686	4	573	44
40	A	1536	41	.0018	.0003	.3308	.0086	1604	9	806	73
	С	1204	19	.0012	.0001	.3084	.0077	1700	4	1479	64
	D	1179	16	.0011	.0001	.3338	.0026	1640	3	1306	44
	E	1215	10	.0009	.0001	.3223	.0019	1697	2	1627	28
	K*	1251	48	.0121	.0036	.2687	.0083	1690	17	413	107
	L*	1193	7	.0048	.0002	.2685	.0013	1690	3	561	- 21
50	Α	1561	42	.0020	.0005	.3344	.0124	1604	9	846	76
	С	1241	22	.0014	.0001	.3104	.0093	1698	5	1394	85
	D	1217	16	.0012	.0001	.3337	.0055	1639	5	1283	87
	\mathbf{E}	1250	9	.0011	.0001	.3231	.0022	1695	3	1555	20
	K*	1282	48	.0138	.0036	.2700	.0084	1690	16	372	93
	L*	1216	7	.0054	.0003	.2656	.0066	1691	3	544	62

^{*}Low-aging piezoelectric ceramic composition.

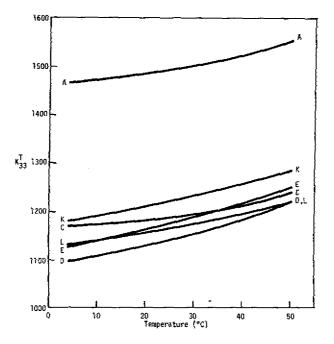


Fig. 2. Relative dielectric constant K_{33}^T as a function of temperature.

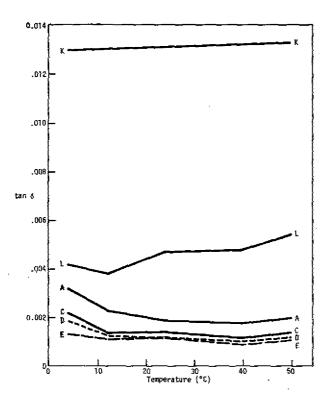


Fig. 3. Loss tangent or dissipation factor tan δ as a function of temperature.

Fig. 4. Effective electromechanical coupling factor $k_{\mbox{eff}}$ as a function of temperature.

Fig. 5. Frequency constant N as a function of temperature.

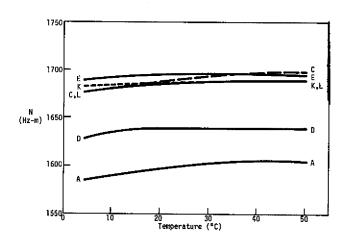
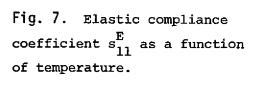


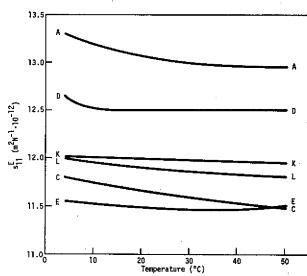
Table III. Elastic compliance coefficient and piezoelectric constants of piezoelectric ceramic samples.

Temp		E s ₁₁	d ₃₁	931
(°C)	Source	$(m^2N^{-1}\times10^{-12})$	(C·N ⁻¹ ×10 ⁻¹²)	(V·m·N ⁻¹ ×10 ⁻³)
4	A	13.29	140.1	10.76
	C	11.79	110.6	10.69
	D	12.64	117.6	12.14
	E	11.55	110.9	11.11
	K*	12.02	95.30	9.18
	<u> 1</u> .*	11.99	94.79	9.47
12	A	13.14	139.3	10.68
	C	11.72	110.1	10.60
	D	12.50	119.4	11.70
	E	11.51	111.8	11.04
	K*	12.01	95.91	9.02
	L*	11.94	94.68	9.37
24	A	13.03	199.5	10.59
	С	11.65	110.7	10.48
	D	12,50	119.9	12.04
	E	11,48	113.7	11.01
	K*	11.96	96.49	8.85
	L*	11.87	95.21	9.27
40	A	12.97	139.0	10.22
	C	11.48	107.9	10.12
	Ď	12.49	120.5	11.55
	E	11.46	113.2	10.52
	K*	11.95	97.83	8.82
	\mathbf{L}^{\bigstar}	11.82	94.87	8.98
50	A	12.95	141.6	10.24
	C	11.51	110.4	10.05
	D	12.50	122.3	11.35
	E	11.52	115.3	10.43
	K*	11.94	99.45	8.76
	Ľ*	11.80	94.70	8.80

^{*}Low-aging piezoelectric ceramic composition.

Fig. 6. Mechanical $Q_{\underline{m}}$ as a function of temperature.





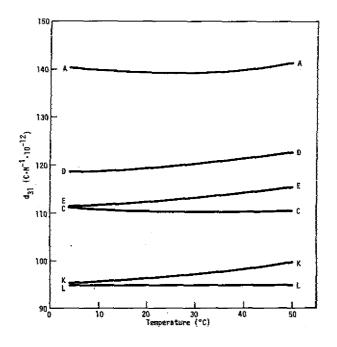


Fig. 8. Piezoelectric constant d₃₁ as a function of temperature.

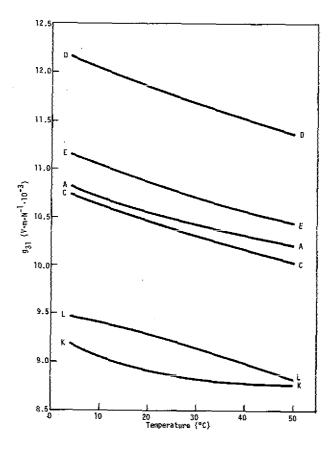


Fig. 9. Piezoelectric constant q_{31} as a function of temperature.

Some interesting deviations from the general spread of the data are seen in the variation of the dielectric constant and the parameters of the low-aging compositions. Figure 2 shows the dielectric constant as a function of temperature and one observes that, except for manufacturer A, the values for products of the different companies and the various compositions are confined to a relatively narrow band. The values of $k_{\rm eff}$, $k_{\rm m}$, $k_{\rm 33}$, $k_{\rm 31}$, $k_{\rm 31}$, and $k_{\rm 11}$ for the two different low-aging compounds also fall within a rather narrow spread.

The relative spread of parameters within a single group (manufacturer) can be ascertained by comparing the standard deviations shown in Table II. Groups A and K, for most cases, exhibit the highest standard deviations and hence the largest spread of values. Groups C and D, for most cases, exhibit a moderate standard deviation. Groups E and L are notable because they exhibit the lowest overall standard deviations, hence the smallest variation from ring to ring produced by the same manufacturer.

The military standard specifies that the variation of the relative dielectric constant shall be limited to a maximum of 7% in the temperature range 0 to 50°C. Table IV shows the percentage change in relative dielectric constant, loss tangent, electromechanical coupling factor, frequency constant, and mechanical Q calculated by finding the percent difference

between the values of the parameters at 0 and 50°C. The change in the relative dielectric constant for these samples exceeds the specified limits for two of the Type I groups, and both of the low-aging compositions exceed the 7% limit. It has been suggested [6] that the specified change in the relative dielectric constant be relaxed to 12%, which would

Table IV. Approximate percent change of parameters with temperature, 0-50°C.

Sou	ırce	каз	tan δ	k _{eff}	N	Q _m
	A	+6.6	-43	-1	+1	+58
	С	+6.5	-38	-3	+1	+49
	D	+11.7	-38	-1	+1	+48
	E	+12.0	-21	-2	0	+26
	K*	+9.5	+2	-1	0	-22
	L*	+8.2	+33	- 3	+1	-4
Average	(Type I)	+9.2	-35	-2	+1	+45
Average (Low-a	aging)	+8.9	+18	-2	+1	-13

^{*}Low-aging piezoelectric ceramic composition.

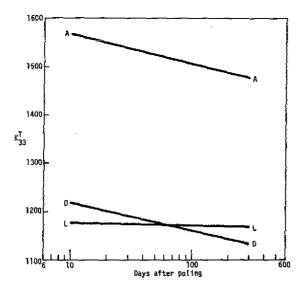


Fig. 10. Aging of relative dielectric constant K_{33}^{T} .

enable all of the groups in this study to satisfy that part of the standard. Table IV shows also that there is considerable variation in temperature rates of change among products from different manufacturers. It is interesting to note that the average values of tan δ , $k_{\mbox{eff}}$, and N given in Table IV are in close agreement with earlier results, but the average values of K_{33}^{T} and $Q_{\mbox{m}}$ are lower [1].

Aging of the relative dielectric constant of the rings was determined by measuring their capacitances at widely separated times. A limited number of the measured aging rates are shown in Fig. 10. Aging rates and ten-day values are presented for Type I ceramic in Table V and for lowaging compositions in Table VI. The majority of the aging rates presented in Table V were taken from an earlier report on Type I ceramic [3]; the remainder are from Fig. 10 and data supplied by manufacturers. It is felt that the aging rates taken from previous work are representative of the present rings because the aging rates taken from Fig. 10 agree closely with previous aging rates [3]. The aging rates presented in Table VI were taken from measurements made by the developers of the low-aging compositions [7,8]. The ten-day values presented in Tables V and VI were determined by extrapolating the room-temperature data points of Figs. 2-9 at the aging rates listed in the tables. It is emphasized that the majority of the aging rates were taken from previous data; thus, the ten-day values presented in Tables V and VI are not intended to be quantitative beyond comparisons with the ranges specified in the military standard.

Table V shows that samples from manufactureres A, C, D, and E generally satisfy the specifications of the military standard, but there are two exceptions: Group A shows an excessive ten-day value for K_{33}^T , and group D shows an excessive aging rate for k_{eff} .

Table V. Approximate aging rates and ten-day values, Type I ceramic samples.

	K	T 33	k	eff		N	s	E 11	á	31	g	31
Source	Aging rate (%)	10-day value	Aging rate (%)	10-day value	Aging rate (%)	10-day value (Hz·m)	Aging rate (%)	10-day value (m ² /N ×10- ¹²)	Aging rate (%)	10-day value (C/N ×10 ⁻¹²)	Aging rate (%)	10-day value (V·m/N ×10-3)
A	-4.0	1568	-1.3	0.3432	+1.0	1576	-2.0	13.43	-4.1	148.2	-0.6	10.68
С	-4.5	1235	-1.3	0.3189	+1.0	1675	-2.1	11.83	-4.8	114.7	-0.1	10.49
D	-4.8	1217	-3.6	0.3591	+0.7	1624	-1.2	12.73	-7.1	133.0	-1.7	12.35
E	-3.3	1213	-1.3	0.3353	+0.7	1681	-1.4	11.68	-3.6	118.7	-0.4	11.06
Average	-4.2	1308	-1.9	0.3391	+0.9	1639	-1.7	12.42	-4.9	128.7	-0.7	11.15
Std. deviation	0.66	173	1.2	0.0167	0.2	49.0	0.44	0.82	1.6	15.0	0.7	0.8
MIL-STD~1376	-6.0	1100- 1400	-2.5	0.310- 0.360	+2.5	1500 - 1750	-	_	-	-	-	-

Table VI. Approximate aging rates and ten-day values, low-aging compositions.

	K	T 33	k	eff		N	s	E 11	đ	31	g	31
Source	Aging rate (%)	10-day value	Aging rate (%)	10-day value	Aging rate (%)	10-day value (Hz·m)	Aging rate (%)	10-day value (m ² /N ×10 ⁻¹²)	Aging rate (%)	10-day value (C/N ×10 ⁻¹²)	Aging rate (%)	10-day value (V·m/N ×10 ⁻³)
K	-0.5	1231	-0.2	0.2676	+0.1	1685	-0.3	12.00	-0.1	96.78	-0.1	8.88
L	-0.6	1175	-0,2	0.2733	+0.1	1684	-0.3	11.91	-0.9	96.18	+0.2	9.25
Average	-0.6	1203	-0.2	0.2705	+0.1	1685	~0.3	11.96	-0.5	96.48	+0.5	9.07
Std. deviation	0.07	40.0	-	0.004	-	0.71		0.06	0.57	0.42	0.2	0.26

Characteristics of the low-aging compositions appear to be similar to those of the Type I ceramic, except for the following:

- a. Mechanical quality factor $Q_{\rm m}$ of the low-aging compositions is considerably lower than that of most of the Type I compositions, although $Q_{\rm m}$ at room temperature (24°C) is greater than 500.
- b. The coupling coefficient $k_{\mbox{eff}}$ for low-aging compositions is below the range of that for Type I compositions.
- c. The loss tangent of low-aging compositions is higher than that of Type I ceramic.
- d. Piezoelectric constants \mathbf{d}_{31} and \mathbf{g}_{31} of the low-aging compositions are lower than those of the Type I ceramic.
- e. The dissipation factor of the low-aging compounds appears to increase as temperature increases, which is the opposite of the effect observed for Type I ceramic.
- f. Mechanical $Q_{\underline{m}}$ of the low-aging compositions decreases with temperature but that of the Type I ceramic increases with temperature.

Table VI points out also that the low-aging compositions are similar to the Type I ceramic. The low-aging compositions meet (indeed greatly exceed) the military standard specifications on aging. The point where the low-aging compositions fail to meet the military standard for Type I ceramic is in their ten-day value of $k_{\rm eff}$. It will be noted also that the ten-day values of $s_{11}^{\rm E}$, d_{31} , and g_{31} are similar to but uniformly lower than those of the Type I ceramic.

Conclusions

Type I Ceramic

Results of the second series of USRD measurements of the low electrical field characteristics of Type I piezoelectric ceramic rings indicate that some progress has been made toward meeting the low electrical field specifications of MIL-STD-1376(SHIPS) as summarized below:

- a. Two of the four groups satisfied the specification on temperature variation of the relative dielectric constant, and the other two were considerably over specified limits. Earlier results were uniformly higher than the limits.
- b. Densities of three groups were on the borderline of the minimum density specification (not significantly different from earlier findings).
- c. Ten-day values of the parameters for all groups were generally within specified limits, as were the earlier ten-day results.

- d. Aging rates appear acceptable with only minor exceptions.
- e. Temperature variation curves for these samples have the same general form as those of the earlier findings.

It has been suggested by the MOST Technical Committee on Transducers and Hydromechanics [6] that both the temperature variation and minimum density specifications be relaxed to 12% and 7.50 g/cm³, respectively. If these changes were incorporated in the military standard, then:

All four Type I groups would meet the temperature variation specification for the dielectric constant.

Only two of the four Type I groups would be borderline on the minimum density specification.

Low-Aging Ceramics

The low-aging compositions measured were generally similar to the Type I composition. The major considerations that prevent the low-aging compositions from satisfying the requirements of the military standard for Type I ceramic are low ten-day values of $k_{\rm eff}$, low densities, and high values of tan δ . Thus it appears that the low-aging compositions could be more nearly classified as a Type I ceramic than as Types II, III, or IV ceramics.

Variation among Products from Different Manufacturers

The variation among products from the different manufacturers was considerable. Exceptions to the general spread of the data observed for most of the parameters are:

- a. Five of the six groups show dielectric-constant-versus-temperature curves that are confined to a relatively narrow band of values.
- b. Parameters of the two different low-aging compositions are confined to a rather narrow range of values.

A large spread of values (i.e., a large standard deviation) was observed within some of the groups. Groups A and K had the largest spread, groups C and D has a moderate spread, and groups E and L had the smallest spread. The large spread of values within a single group possibly could be reduced by better quality control by the manufacturers.

Acknowledgments

Thanks are due to Pamela Pasik for her efforts in collecting the data upon which this report is based.

References

- [1] R. W. Timme, "Low Electrical Field Characteristics of Piezoelectric Ceramic Rings," NRL Report 7528, 5 Jan 1973 [AD-907 068L].
- [2] MIL-STD-1376(SHIPS), "Piezoelectric Ceramic for Sonar Transducers," 21 Dec 1970.
- [3] G. E. Martin. R. W. Lewis, and R. A. Creswell, "Evaluation of Standard Navy Type I Piezoelectric Ceramics," Naval Undersea Center TN 896, Dec 1972.
- [4] C. LeBlanc, "NUSC Measurements on Standard Navy Type I Ceramic," Naval Underwater Systems Center TM No. TD12-469-73, 12 Nov 1973.
- [5] P. L. Smith and R. Pohanka, "Characterization of Navy Type I Ceramic," NRL Letter Report (in preparation).
- [6] Materials Panel MOST Technical Committee on Transducers and Hydro-mechanics, "An Evaluation of Commercial Navy Type I Sonar Ceramics," Naval Sea Systems Command, Aug 1974.
- [7] J. C. Kyonka, "Development of High Drive Stable Piezoelectric Ceramic," Honeywell Ceramics Center, Government and Aeronautical Products Division, Contract No. N00024-72-C-1173, Naval Sea Systems Command, undated.
- [8] B. Jaffe, "Development of a Stable Piezoelectric Ceramic for Sonar," Vernitron Piezoelectric Division, Contract No. N00024-72-C-1174, Naval Sea Systems Command, 14 Jan 1974.
- [9] D. A. Berlincourt, D. R. Curran, and H. Jaffe, "Piezoelectric and Piezomagnetic Materials and Their Function in Transducers," in Physical Acoustics, W. P. Mason, ed. (Academic Press, New York, 1964), Vol. I, Part A, p. 221.

Appendix A

Code for Identifying Sources of Piezoelectric Ceramic Material

Type I

A	Channel Industries
С	Gulton
D	Honeywell
E	Vernitron
	Low-Aging Composition

Honeywell K L Vernitron